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13. ABSTRACT (Maximum 200 words)

The goal of this project was to develop shape memory alloys with transition temperatures above 100°C. The main focus was on TiNiHf. Special vacuum sputtering setups were used to produce thin films having variations in composition, ranging from those rich in Ti+Hf to those rich in Ni.

Three targets were used: TiNi, Hf, and Ni. Deposition rates were calibrated separately for each target. These calibrations were used to calculate composition of film deposited by simultaneous sputtering from all three targets. Although this procedure does not permit measurement of absolute composition, it makes possible a methodical search for alloys with increased transition temperature and improved ductility by systematic and controlled variation of composition. Depositions were done with predicted alloy compositions close to 50 at% Ni, the balance being Ti+Hf. The Hf concentration was varied within the range 10 - 15 at%.

TiNiHf films were produced having transition temperatures above 100°C, with austenite finish temperatures as high as 170°C. Measurements of phase transformation temperature, ductility, and composition were made. High ductility and shape recovery up to 4 percent was achieved. Micromachined valve actuators were fabricated and tested. Actuators demonstrated thermomechanical performance similar to that of binary TiNi film.

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The Contractor, TiNi Alloy Company, hereby declares that, to the best of its knowledge and belief, the technical data delivered here with under Contract No. DAAH01-01-C-R125 is complete, accurate, and complies with all requirements of the contract.

Date: Oct. 23, 2001

Name and Title of Authorized Official: A. David Johnson, Principal Investigator

Phase I Technical Objectives

Questions Addressed in Phase I

As stated in the Phase I proposal, the overall objectives of this research are to find compositions of TiNiHf and TiNiPd alloy having shape recovery properties similar to binary TiNi but with martensite transition temperatures above 100°C and austenite transition temperatures greater than 150°C; and to fabricate prototype actuators from one or more of these alloys.

These questions were addressed:

What compositions of TiNiHf and TiNiPd produce the highest austenite and martensite transformation temperatures?

Alloy composition nominally for 10 at% Hf, 52.4 at% Ni, 37.6 at% Ti showed an austenitic transition temperature of 170°C. (Table I, Run number 121, sample #14) In several experiments with sputtered TiNiPd, an elevated phase transformation was observed but all samples had poor ductility.

What compositions yield the smallest hysteresis?

TiNiHf in the ratio ~38:52:10 at% showed a hysteresis of 20°C, comparable to binary TiNi. (Run Number 121, sample #15)

Are there compositions that are sufficiently ductile to make microdevices?

Shape recovery of 4% was measured on film from the deposition Run #121 (~Hf 10 at%, Ti 38 at%, Ni 52 at%).

Valve actuators were micromachined and operated, with good results.

What modifications to our normal fabrication procedures must be made in order to fabricate functional microactuators?

Methods of photolithography and chemical micromachining were used successfully without significant modification.

Proposed Steps to Accomplish Objectives

The proposed steps to accomplish these objectives were:

- 1) Sputter deposit TiNi-based shape memory thin film samples with addition of up to 30 at% Hf (replacing Ti) or 20 at% Pd (replacing Ni).

TiNi, Hf, and Ni were co-sputtered from three separate targets, with compositions of up to 15 at% Hf.

- 2) Heat treat the film to produce an austenite/martensite crystalline system.

All annealing was done at 500+°C.

- 3) Measure transition temperatures by resistivity and differential scanning calorimetry (DSC).

Extensive resistivity measurements were made, showing a range of transition temperatures.

No DSC measurements were made in Phase I. The vendor used in past experiments (Thermal Options in Escondido, CA) is no longer available. No new vendor was engaged in time to include results in this report.

- 4) Measure stress-strain-temperature isotherms on small specimens taken from the substrates.

It was not necessary to make small specimens, as film of nearly uniform composition was deposited on large portions of 4-inch wafer surfaces. Sample sizes used were 1 mm by ~30 mm.

- 5) Using inductively coupled plasma mass spectroscopy (ICPMS) or other analytical tools, measure compositions of specimens of ternary alloys exhibiting martensitic structure and plastic deformation in stress-strain isotherms.

Only very limited ICPMS analysis was available for Phase I. Energy dispersive spectrometry (EDS), wave dispersive spectrometry (WDS), and Auger measurements were done on a limited number of film samples.

- 6) Test specimens for ductility by peeling film from substrates.

Highly ductile, non-brittle films were removed from substrates using an etched 1000 Å Cr sacrificial layer. These were mounted and tested on a stress-strain fixture with load cell and LVDT to measure force and displacement. Shape recovery as high as 4% was measured. The stress required to induce plastic

deformation was higher than for binary TiNi, otherwise the thermo-mechanical behavior of TiNiHf is similar to TiNi film.

Mechanical behavior was further confirmed by fabricating and testing devices in the form of valve actuators.

Preliminary results were also obtained on some objectives originally relegated to Phase II, namely:

- 7) Explore the hypothesis that the best shape memory properties are developed in alloys that are Ni(50 at%), (Ti + Hf)(50 at%) i.e. with Hf added; or Ti(50 at%), (Ni + Pd)(50 at%) i.e. with Pd added.

This hypothesis is strongly indicated to be correct from the findings of Phase I research. All films demonstrating high transition temperature and ductile mechanical characteristics were ~50 at% Ni within our ability to measure composition.

- 8) Explore the use of Cu addition to replace Ni as a means of spreading out the transition temperature thereby increasing the range of temperatures over which the alloy is ductile.

This possibility was not explored in Phase I due to lack of appropriate targets.

- 9) Explore the effects of differing substrate temperatures on stress-strain-temperature behavior.

The results from a limited set of experiments indicate that heating the substrate causes columnar structures in the film. Poor adhesion between these structures causes the film to be weak and brittle. At temperatures below crystallization (500°C) the columnar structure appears to result from propagation of surface imperfections. When substrates were held at temperatures above 500°C, which was considered desirable to save the separate crystallization process step, the result was extremely brittle material. It is hypothesized that in the formation of the initial layers, islands of crystalline TiNiHf are formed, and these act as imperfections upon which the columnar structures grow as an epitaxial process.

- 10) Make scanning electron microscope (SEM) examination of samples for granularity, columnar structure, and other indications of imperfect crystal structure.

In Phase I many SEM pictures were made. SEM was used as a tool in all stages of the research effort. In Phase II X-ray diffraction (XRD) and transmission electron microscopy (TEM) will also be used to examine the crystal structure for precipitates and to determine if there are additional phases present in the matrix.

- 11) Prepare a set of tables summarizing the results in terms of transition temperature, strain recovery, ductility, and composition.

A summary of Phase I results are shown in Table I below.

Run#	Ti, at%	Ni, at%	Hf, at%	Af max,C	Mf max,C	Mechanical Characteristics
112	34.3	51	14.7	165	85	Too brittle to characterize
113	36	50	14	160	80	"
114	35.3	50.7	14	170	95	"
115	36.8	49.2	14	145	65	"
117	38.5	47.5	14	140	50	"
118	33.2	52.5	14	180	120	"
121	37.6	52.4	10	160	90	Shows plastic deformation
123	38	52	10	150	85	Good stress-strain measurements
125	38.2	51.8	10	150	80	Somewhat brittle
126	39	51	10	145	80	"
129	38	51	11	140	75	Sample made: not ductile
130	40	51	9	140	75	Ductile, some plastic deformation
131	38	52	10	Same as 123		Actuator devices fabricated & tested
132	40	51	9	Same as 130		Actuator devices fabricated & tested

Table I. Results of a series of sputtering runs. TiNiHf film was produced by co-sputtering as discussed below. Small changes in composition affect the transformation temperature and ductility of the produced film. Sufficiently good control of composition was achieved that devices were made and tested.

12) Fabricate dies with microactuators of high temperature alloy film and demonstrate performance of fiber optic switches.

Microactuator dies were fabricated and operated as valve actuators: application to fiber optic switches has been postponed.

13) Document all processes and experimental results.

Experimental Approach--Overview

The project goal is to produce alloys with useable shape memory properties having transition temperatures well above 100°C. Binary alloys containing TiNi have good thermo-mechanical properties but transition temperatures limited to less than 100°C. Alloys of TiNiHf and TiNiPd have been shown to have transition temperatures up to 300°C but these have not been commercially acceptable because they are generally brittle and difficult to fabricate into devices. We have undertaken to investigate the mechanical/thermal properties of a continuum of compositions to determine which have useful properties for making actuator devices.

There are three kinds of experimental challenges:

- There is no way to know *a priori* what compositions will produce optimum thermo-mechanical characteristics;
- Reproducible results are difficult to achieve because a composition variation of 0.1 % can have a noticeable effect: holding chemical composition to such small tolerances is difficult; and
- Measurement of composition of small specimens of material to 0.1% can be accomplished only with highly skilled use of expensive apparatus.

The early strategy adopted was to sputter deposit film samples with varying composition (on silicon wafers) by adding small quantities of excess pure Ti, Ni, Hf, Pd and possibly Cu to the sputter-deposited film. These film samples were to be subjected to the following tests:

- Visual test (film that is martensitic at room temperature has a characteristic cloudy surface due to the shape change in the crystals during the transformation);
- Resistivity versus temperature measurement (the high-temperature phase has a different temperature dependence than the martensite); and
- Mechanical characterization (strength and ductility).

These early experiments produced some useful results, but also revealed major shortcomings of the technique. The deposition rate from pieces placed on the target caused nearly uncontrolled composition variation over very small distances. Variation of composition also had a radial component due to inherently different sputtering rates for Ti and Ni. The result was that most of the wafer was covered with material that was so far from the optimum composition that it was not informative.

To overcome these limitations a different strategy was adopted. A sputtering system with accurate control of power enabled co-sputtering from three separate targets simultaneously. Much improved results were obtained using this co-sputtering technique, so that a majority of the goals were achieved.

Chronology of Early Sputtering Experiments and Preliminary Results

This section contains a description of experiments done early in the program, leading up to the use of co-sputtering.

Results of Sputtering From TiNiHf and TiNiHfCu Targets.

Two types of targets (both 4-inch diameter) were used. The first, Ti 28.9 wt%, Ni 44.2 wt %, Hf 26.9 wt %, was purchased from Alex Popoff at Metaltex Corp. The second, Ti 32.7 wt% , Ni 35.6 wt%, Hf 27 wt%, Cu 4.7 wt%, was fabricated by Anatoli Danilov in St. Petersburg, Russia.

Film deposited from the TiNiHf target, without additions, was brittle and no phase transition was detected. Several experiments were performed with additions of varying amounts of Ni, Hf, and Ti. Addition of Hf (and Ti) produced some very small samples of film with high transition temperature (up to 240°C) but these samples all had very wide temperature hysteresis. Some limited degree of ductility was observed, but no stress-strain measurements were undertaken because of the small sample size.

These results suggest that Ti and Hf are selectively lost during deposition. Adding Ti cannot raise the transition temperature, and addition of Hf creates rapidly varying gradients, so that the regions containing martensite are very small.

Film deposited from the TiNiHfCu target without additions also was very brittle so that no measurement was undertaken. However, addition of Hf produced a region of film with a halo, and this region, when analyzed with ICPMS (see below) does obey the 50-50 rule. The reason for poor results when this target was used probably stems from the very high content of Ni, and lower than expected Hf content as determined by ICPMS, so that useful samples of film were obtained only by chance.

TiNiPd Deposition

The target used for all TiNiPd deposition runs was obtained from Armada. Its composition was measured by NASA Lewis Cleveland to be 38 wt% Ti, 22 wt%Ni, 37 wt% Pd. Small amounts of Si and Fe were found.

The target containing TiNiPd by itself produced only samples so brittle that they peeled from the substrate during cool-down from crystallization. Chemical analysis of the target suggests that the percentage of Pd is sufficiently high so that the combination of Pd with Ni is much greater than 50 atomic percent. Results from a sputtering run with a TiNiPd target and 4 pieces of Ti added are shown in Figure 1 below.

Two resistivity traces are shown for samples taken from different parts of the wafer. The one labeled Sample #7 shows a transformation above 100°C with a small hysteresis (<10°C). Unfortunately the material was too brittle for stress-strain measurements.

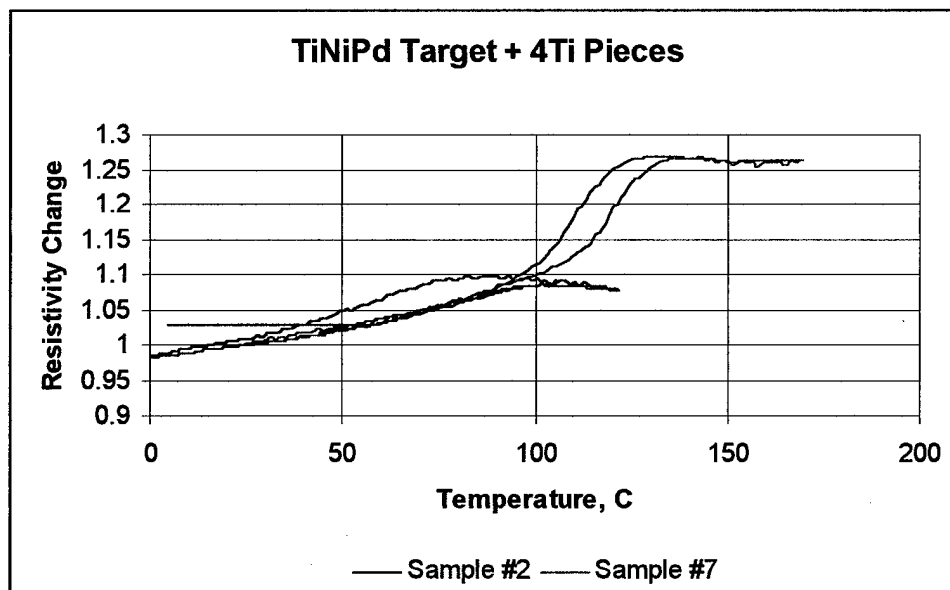


Figure 1. Two resistivity traces for thin film sputter deposited using a TiNiPd target. Samples taken from different parts of same wafer.

Heated Substrate Experiments and Results.

One of the tasks described in the proposal was to incorporate a substrate heater in the sputtering system so that thin alloy film can be deposited at a high enough temperature to produce crystalline material without annealing. A successful outcome would obviate the need for a separate heat-treatment process step.

A square substrate support approximately 15 x 15 cm was constructed of two pieces of stainless steel with an electric resistance heater sandwiched between. This was equipped with a thermocouple and feedthrough cables to operate within the NRC vacuum sputtering system.

In the initial experiment, TiNi film was deposited while the substrate was maintained at an elevated temperature measured at 500°C. The result was positive, showing a 'halo' over a large part of the surface, indicating that most of the wafer was coated with martensite material, and demonstrating that deposition of binary material on a heated substrate produced crystalline material without the usual annealing process.

Resistivity measurements also indicate that the transition temperature was normal, showing a typical hysteresis curve attributed to an intermediate 'R'-phase. However, mechanical properties of this film were not desirable: when the material was separated from the substrate and an attempt was made to mount it for stress-strain measurement, it fractured. When the fractured surfaces were examined in the SEM, they revealed a columnar structure with poor intracrystalline adhesion resulting in a lack of strength. A tentative explanation is that islands of material first condensed on the substrate surface, and these nucleated into micro-crystals. Subsequent deposition on the hot surface caused individual crystals to grow epitaxially from

these micro-crystals through the film, resulting in columnar structure and poor adhesion of the crystals to each other.

Figure 2 shows two views of a fractured edge of TiNi deposited upon a heated substrate.

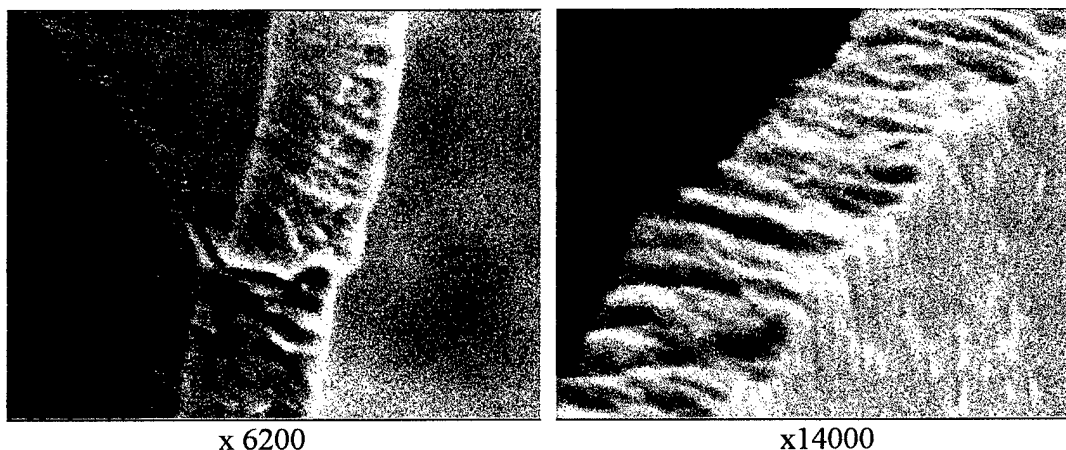


Figure 2. Scanning electron beam pictures of a sample of TiNi film deposited on a substrate that was heated to 500°C. The crystal structure has columns perpendicular to the surface, and these columns do not adhere strongly to each other, resulting in brittle fracture of the film when it is deformed. The film is approximately 2 microns thick.

Co-Sputtering of TiNi, Hf, and Ni

After the preliminary experiments described in the previous section, which did not produce satisfactory results, a different tack was taken, namely co-sputtering from three targets. The strategy is to start with a TiNi target known to produce film with very nearly 50 at% Ni and Ti, add Hf from a second target to raise the transformation temperature, and add Ni from a third target so as to balance the added Hf and keep the content of Ni at ~50 at% to preserve ductility in the film. A series of sputtering deposition runs were done with varying amounts of Hf and Ni.

The results from this series were a significant improvement. Operating conditions were sufficiently well controlled from run to run that experimental results were repeated from day to day. A systematic study shows that the 50-50 rule is validated. It was confirmed that composition variation of less than one percent alters the mechanical behavior and thermal phase-change temperature dramatically. The compositions were calculated from the measured sputtering rates. EDS was used to measure variation of the components from place to place on the substrate (a method known as 'mapping') and, within experimental error, it confirmed the predicted compositions. It has not been feasible to measure the absolute composition with accuracy greater than about plus or minus 1%.

Film was produced with transition temperatures as high as 170°C. Ductility, which had been lacking in previous experiments, was clearly demonstrated. Specimens subjected to stress-strain-temperature measurement showed shape recovery as high as 4 %. Functional valve actuators were fabricated and demonstrated, and these had sufficient stroke and force output for practical applications.

Description Of Experimental Procedures Used In Co-Sputtering TiNiHf Material

The procedure employed, co-sputtering from three targets, relies on stability of power supplies and reproducibility of vacuum conditions. The sputtering system used, a Perkin-Elmer 4450 prepared by Thin Film Equipment Services, Santa Clara CA. is equipped with highly stable and accurate pumps, power supplies, and instrumentation.[1] The results achieved were made possible by use of this improved system.

Sputtering Conditions and System Configuration

The Perkin-Elmer vacuum system is evacuated by a CTI-Cryogenics high-vacuum pump backed by a Leybold Trivac roughing pump. Base pressure attained is $2-5 \times 10^{-7}$ Torr. Sputtering is at an Ar pressure of 2×10^{-3} Torr.

The primary sputtering source is an eight-inch TiNi target (purchased from Alex Popoff, Metaltex Corp.) in a direct-current magnetron with a custom rotating magnet assembly (built by Carl Palmucci Associates), powered by a 5 kW Perkin-Elmer Programmable Power Regulating DC magnetron supply.

The second source is an 8-inch Hf target (from Sputtering Materials) in a fixed-magnet Perkin-Elmer DC magnetron. Power is supplied by an Advanced Energy Industries Inc. model MDX 1kW magnetron drive, provided by Cougar Laboratories, Fremont CA.

The third source is an 8-inch Ni target in a radio-frequency sputterer powered with an ENI ACG-6B RF plasma generator with an output power limited to about 600 watts.

Calculation of Sputtering Power Settings to Produce Film of Desired Composition.

Composition of the deposited film was predicted from measurements of deposition rates from each of the three targets, adjusted for power supplied to each target. This is shown in Figure 3. The estimated error in thickness measurement is 2%. Variation across a wafer due to geometric effects may be as much as 5%.

The main constraint that we intended to impose is that the resulting deposited film should be 50 atomic percent Ni and 50 atomic percent Ti + Hf. For this purpose, measured thickness deposition rates are converted to molar deposition rates.

The actual (thickness) deposition rate for atomic species (i) is R_i = Rate measured at full power. If deposition rate is assumed to be directly proportional to power, the actual deposition rate R_{a_i} is

actual power divided by full power multiplied by rate measured at full power. For improved accuracy, four deposition rates were measured, at four power settings, and a curve was fitted to these points. The resulting formula was used to interpolate actual sputter deposition rates.

For each atomic species, the number of moles deposited per unit time per unit area is

$$M_i = Ra_i * \text{Density}_i / \text{Atomic wt.}_i$$

Atomic fraction for each species i is then

$$F_i = M_i / \text{Sum}\{ M_i \}$$

For Ti and Ni deposition rates from the TiNi target, the deposition rate and density for TiNi are used, and the rate is multiplied by the weight fraction of Ti or Ni respectively.

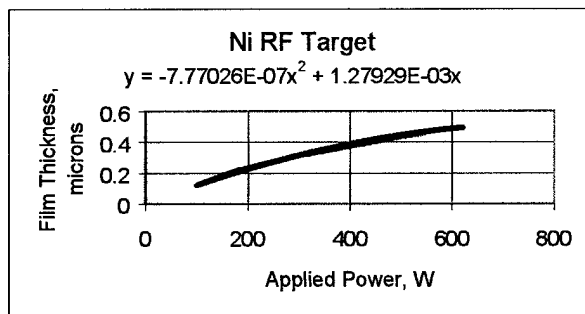
Results of this calculation are shown in Table II for several compositions used in a series of sputtering runs.

Calibration of Sputtering Rate versus Power for Three Targets

Power,watts Thickness,microns, deposited in 60 minutes

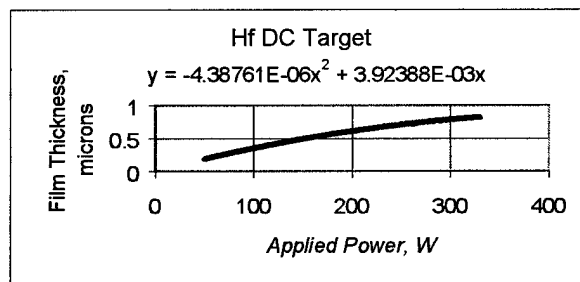
620	0.5
400	0.37
200	0.24
100	0.125

Ni RF Target



330	0.82
200	0.6
100	0.35
50	0.2

Hf DC Target



2000	2.2
1500	1.85
1000	1.25
500	0.7

TiNi DC Rot.Mag.

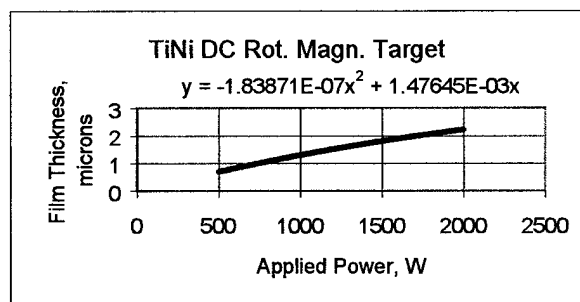


Figure 3. Calibration of sputtering rate versus power for three targets.

COSPUTTERING CALCULATIONS; TiNi + Ni + Hf USING LSQ FIT TO 4 POINTS TO CALC. DEPOSITIONRATE								
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	Weight	Meas'd	Meas'd	Density	At. Wt.	CalcDepRate		
INPUT	Fraction	DepRate	Power	Gm	Z	asMeas.		
PARAMETERS		$\mu\text{m}/\text{Hr}$	Watts	$/\text{cm}^3$				
TiNi (Target 1, DC RotMag)		2.2	2000	6.4			SumTi+Ni	
Wt. Fraction Ti	0.44			4.5	47.88	0.9746	2.2150	
Wt. Fraction Ni	0.56			8.9	58.69	1.2404		
Ni (Target 2, RF)		0.5	620	8.9	58.69	0.4944		
Hf (Target 3, DC Magnetron)		0.82	330	13.3	178.49	0.8200		
By Run Number	Power, Watts			Calculated Dep.Rates, Microns/hr				
QUANTITIES	Target 1	Target 2	Target 3		Ti(1)	Ni(1)	Ni(2)	Hf(3)
	TiNi	Ni	Hf					
Run #99	2000	186	170		0.975	1.241	0.211	0.540
Run #100	2000	186	185		0.975	1.241	0.211	0.576
Run #101	2000	420	300		0.975	1.241	0.400	0.782
Run #102	1500	420	300		0.792	1.008	0.400	0.782
Run #103	1000	420	300		0.568	0.724	0.400	0.782
Run #104	2000	450	322		0.975	1.241	0.418	0.809
Run #105	2000	380	270		0.975	1.241	0.374	0.740
Run #113	2000	290	250		0.975	1.241	0.306	0.707
Run #114	2000	350	260		0.975	1.241	0.353	0.724
Run #115	2000	240	240		0.975	1.241	0.262	0.689
Run #117	2000	150	230		0.975	1.241	0.174	0.670
Run #118	2000	570	290		0.975	1.241	0.477	0.769
Run #120	1200	600	185		0.663	0.843	0.488	0.576
Run #121	2000	300	150		0.975	1.241	0.314	0.490
Run #122	2000	300	150		0.975	1.241	0.314	0.490
Run #123	2000	280	149		0.975	1.241	0.297	0.487
Run #125	2000	265	147		0.975	1.241	0.284	0.482
Run #126	2000	220	145		0.975	1.241	0.244	0.477
Run #129	2000	250	167		0.975	1.241	0.271	0.533
Run #130	2000	185	120		0.975	1.241	0.210	0.408
Run #131	2000	280	149		0.975	1.241	0.297	0.487
Run #132	2000	185	120		0.975	1.241	0.210	0.408
	Deposition Rate			Atomic Fraction				
	Moles/hr/micr^2		*1.0e12					
	Target 1	Target 1	Target 2	Target 3				
	Ti(1)	Ni(1)	Ni(2)	Hf(3)	Ti(1)	Ni(1)	Ni (2)	Hf(3)
Run #99	0.130	0.135	0.032	0.040	0.386	0.400	0.095	0.119
								0.505

Run #100	0.130	0.135	0.032	0.043	0.383	0.397	0.094	0.126	0.509
Run #101	0.130	0.135	0.061	0.058	0.339	0.352	0.158	0.152	0.490
Run #102	0.106	0.110	0.061	0.058	0.316	0.328	0.181	0.174	0.490
Run #103	0.076	0.079	0.061	0.058	0.277	0.288	0.222	0.213	0.490
Run #104	0.130	0.135	0.063	0.060	0.335	0.348	0.163	0.155	0.489
Run #105	0.130	0.135	0.057	0.055	0.345	0.359	0.150	0.146	0.491
Run #113	0.130	0.135	0.046	0.053	0.357	0.371	0.127	0.144	0.502
Run #114	0.130	0.135	0.053	0.054	0.349	0.363	0.143	0.145	0.494
Run #115	0.130	0.135	0.040	0.051	0.365	0.379	0.111	0.144	0.509
Run #117	0.130	0.135	0.026	0.050	0.381	0.396	0.077	0.146	0.527
Run #118	0.130	0.135	0.072	0.057	0.330	0.342	0.183	0.145	0.475
Run #120	0.089	0.092	0.074	0.043	0.298	0.309	0.249	0.144	0.442
Run #121	0.130	0.135	0.048	0.037	0.373	0.387	0.136	0.104	0.477
Run #122	0.130	0.135	0.048	0.037	0.373	0.387	0.136	0.104	0.477
Run #123	0.130	0.135	0.045	0.036	0.376	0.390	0.130	0.105	0.480
Run #125	0.130	0.135	0.043	0.036	0.378	0.393	0.125	0.104	0.482
Run #126	0.130	0.135	0.037	0.036	0.385	0.400	0.109	0.105	0.490
Run #129	0.130	0.135	0.041	0.040	0.376	0.391	0.119	0.115	0.491
Run #130	0.130	0.135	0.032	0.030	0.397	0.413	0.097	0.093	0.490
Run #131	0.130	0.135	0.045	0.036	0.376	0.390	0.130	0.105	0.480
Run #132	0.130	0.135	0.032	0.030	0.397	0.413	0.097	0.093	0.490

Table II. Co-sputtering calculations for TiNi + Ni + Hf using least squares fit to 4 points to calculate deposition rates from the individual targets.

Discussion

Film was sputter-deposited according to the parameters listed in Table II above.

The results can be summarized as follows:

TiNiHf film having high transition temperature, good ductility, and useful shape recovery was produced.

Resistivity measurements show phase transformations with austenite finish (A_f) temperatures as high as 170°C and positively correlated with Hf content.

Film was produced that was ductile enough to be removed from the substrate. Stress-strain measurements were made showing shape recovery of up to 4 percent.

Actuators were micro-fabricated using MEMS processes. These actuators were tested in pneumatic valves, and the resulting flows demonstrate that the high-temperature TiNiHf film produces displacement and force comparable to TiNi films.

Characterization of TiNiHf Film: Resistivity, Composition, Stress-Strain, and Actuation

A large number of data sets were taken with co-sputtered TiNiHf film. Several of the sputtering runs, especially the early ones, did not produce useful properties. Representative samples showing desirable characteristics have been chosen for discussion from three runs: #123 (resistivity and composition but no stress-strain); #121 (stress-strain); #132 (actuator dies performance). These runs are near the same composition but have been processed differently in order to obtain the differing types of data.

	Composition, atomic percent				
	Loc.1	Loc.2	Loc.3	Loc.4	Loc. 5
<u>Calculated</u>					
Nickel	52.0	52.0	52.0	52.0	52.0
Titanium	37.6	37.6	37.6	37.6	37.6
Hafnium	10.5	10.5	10.5	10.5	10.5
<u>EDS</u>					
Nickel	49.1	49.5	49.9	49.4	49.2
Titanium	40.6	40.9	40.7	40.1	40.0
Hafnium	10.3	9.6	9.5	10.5	10.8

Table III. Comparison of resistivity and composition for run #123. Composition was measured at five locations across the wafer starting at the major flat. Composition was determined by calculation from deposition rates, and by energy dispersive spectrometry.[2] Auger spectroscopy results have not been completed.[3]

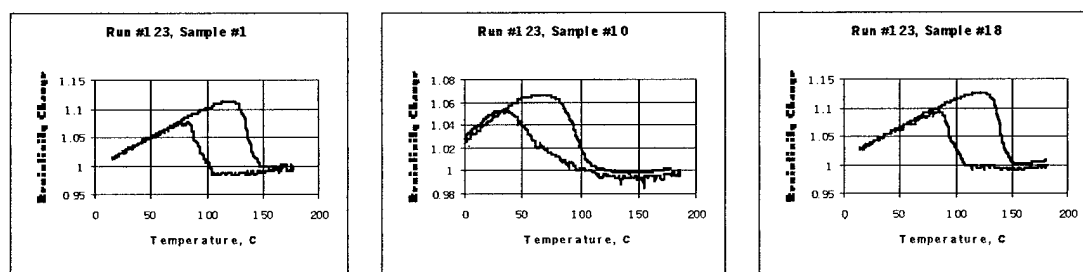


Figure 4. Resistivity versus temperature measured at three locations: near Loc.1, Loc.3, Loc.5

Figure 4 shows the results of measuring resistivity at three locations on the same substrate for which composition measurements are shown in Table II. This example demonstrates that there was variation of composition across the wafer, some of which is expected from geometrical considerations (the targets were not shielded). Also, it is known from other experiments that the central portion of films sputtered from a binary TiNi DC magnetron target are enriched in Ni. This variation is reflected in phase transformation temperatures as measured by resistivity. However, measurement of composition by EDS, shown in Table IV, illustrates the difficulty of

correlating composition measurement with measurement of resistivity: all measurements of composition from five locations on the substrate are consistent within experimental error, but significant and systematic differences are seen in resistivity. A more accurate means of composition measurement is needed if useful bulk materials are to be produced.

Loc	Ti at%	Ni at%	Hf at%
#1-1	39.4	50.1	10.6
#1-2	40.6	49.1	10.3
#1-3	39.7	49.9	10.4
#2-1	39.4	49.4	11.2
#2-2	40.6	49.8	9.6
#2-3	40.7	49.5	9.9
#3-1	40.4	51	8.6
#3-2	40.2	50.2	9.6
#3-3	40.5	48.7	10.8
#4-1	40.9	48.8	10.4
#4-2	40.3	50.4	9.3
#4-3	40.1	50.3	9.6
#5-1	40	49.2	10.8
#5-2	39.5	50	10.5
#5-3	41	48.7	10.3

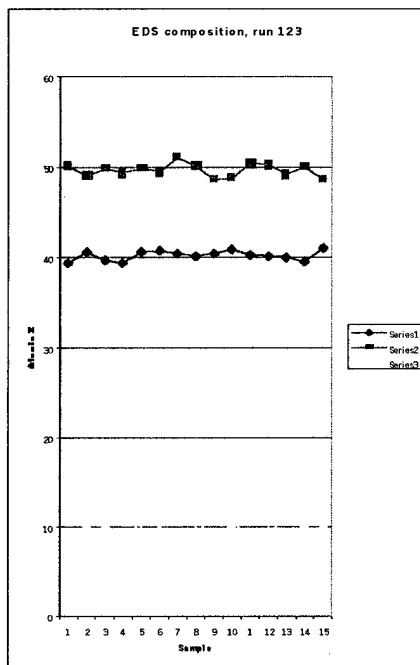


Table IV. Three EDS measurements were taken at each of five locations across the substrate diameter. Ni content is near 50, Ti near 40 and Hf near 10 at%. All deviations are within expected error for this type of spectrometry: however, resistivity measurements show significant deviations in phase transformation temperature at these same locations.

Figure 5 contains data from measurement of stress versus strain. Force was measured using a load cell and displacement using a linear variable differential transducer (LVDT). This plot shows that the sample tested has a shape recovery of nearly 4 percent, and the two slopes are consistent with elastic and plastic deformation of martensite. It is worth noting that the stress required for the deformation of martensite in TiNiHf film is higher than that for binary TiNi. Whether this is an inherent characteristic of ternary alloys or results from precipitates or other transformations is not known at this time, but will be the subject of additional study in Phase II.

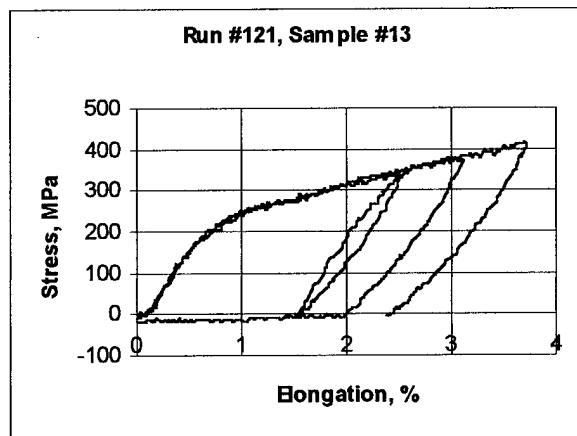


Figure 5. Stress-strain plot for ductile material, run #121.

Figure 6 is a photograph of several actuators formed by micromachining of silicon and TiNiHf. Each actuator consists of a rectangular frame of silicon, 8 mm long and 5 mm wide, a central poppet etched from the same single crystal silicon wafer as the frame, and four microribbons of TiNiHf that connect the frame and the poppet. When a force is exerted perpendicular to the plane of the frame, the poppet moves and the TiNiHf microribbons are stretched longitudinally. When an electric current passes through the microribbons it generates Joule heat, the TiNiHf transforms to austenite, contracts and moves the poppet back into the plane of the frame.

A valve is formed by mounting this actuator on an orifice die with a spacer, and applying a bias force to press the poppet against the orifice. Air pressure is applied to the orifice, and flow through the orifice is measured with a conventional flow meter. Flow rates as high as one liter per minute were recorded with current of 150 milliamperes applied to the actuator. This result is consistent with the performance of TiNi actuators except for a required increase of current, as expected since the transformation temperature is higher.

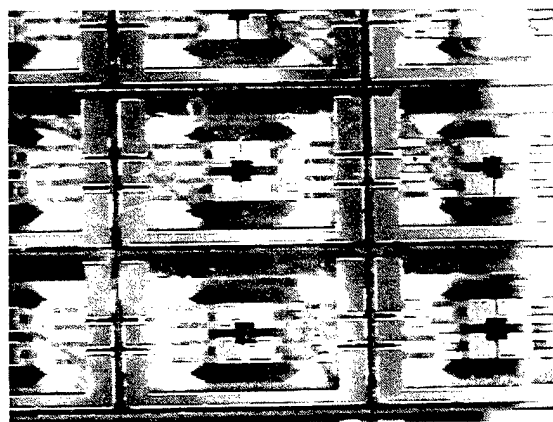


Figure 6. Actuators formed by micromachining of silicon and TiNiHf.

From the geometry of the actuator, the strain can be derived to be:

$$(L + \Delta L)^2 = d^2 + L^2$$

where L = length of microribbon

ΔL = change in length of microactuator

d = displacement of the poppet

Since strain is defined as $\Delta L / L$

It follows that $\text{Strain} = d^2 / 2L^2$.

From the measurement, taking $L = 1\text{mm} = 0.04\text{ inches}$, the strain recovered is approximately 1%.

Figure 7 shows the result of measuring displacement versus actuation current at constant force. Force was measured using a load cell. An approximately constant force was applied by means of a bias spring more than an inch long. During the period this force was sustained, the displacement was measured with an LVDT while the actuation current was increased to a maximum, and then decreased to zero. Force, displacement, and current were measured and recorded by National Instruments hardware and LabView software operating on a Pentium microprocessor computer.

These results demonstrate that repeatable cycles are achieved and that the displacement is as expected for the length of TiNi microribbon.

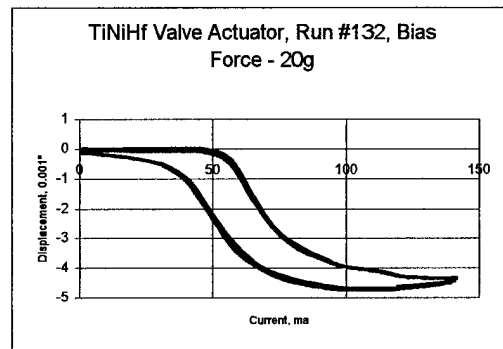


Figure 7. Result of measuring displacement versus actuation current at constant force.

Discussion

Results show that the film with nominal composition Ti(40 at%)Ni(50 at%)Hf(10 at%) has a transition temperature above 100°C, forceful shape recovery, and sufficient ductility to be fabricated into devices.

Stress-strain data from the samples studied show that TiNiHf film requires higher stress to achieve a martensite plateau than does TiNi. The material is considerably more stiff than binary

TiNi. It is possible that other phases may be present. Part of the Phase II effort will be to study this using X-ray diffraction and transmission electron microscopy and to better understand the crystal structure.

The increased stiffness may be due to precipitates. These may change if annealing conditions are varied. Annealing was done by bringing samples to 500°C or slightly higher by thermal heating on a hot plate in vacuum (5×10^{-6} Torr), and allowing to cool over a time of approximately 3 hours. This long time for cooling may permit precipitates to form, causing stiffness. In this case it should improve the mechanical characteristics if the heating is done for a short time, i.e. by infrared (IR) heating. On the other hand, it may be that the material is incompletely crystallized at 500°C, in which case heating to a higher temperature should alter the behavior. These experiments were not completed in Phase I.

Although our procedure for deposition, using three targets, has reduced the composition variation across a substrate surface, it has not completely eliminated it. This is seen when resistivity measurements are made on samples taken along a diameter of the wafer substrate. In one example the variation is from $>100^\circ\text{C}$ at the periphery to $<10^\circ\text{C}$ in the center. In subsequent runs the amount of Ni was decreased in increments of 0.2 at%. The transition temperature at the periphery remained almost constant while that in the center rose to 50°C , then to 100°C . The transition temperature at the periphery remained almost constant for these compositions, but decreased when the content of Ni was increased by 0.6 at%. These results illustrate the extremely narrow control of composition that must be maintained to achieve desirable physical characteristics.

The composition is indeed critical. This can be seen although the method used to control Hf content, based on dead-reckoning, is somewhat crude: the sputter deposition rate for each component is measured, and the composition controlled by the power applied to the three sputtering sources: TiNi DC rotating magnet, HF DC, Ni RF. Table I shows that a changes of one to two percent content of any one of the three components has the power to change the material characteristics from brittle with no detectable phase transformation to a material with a transformation above 100°C and with good ductility.

Remaining Questions that Require Answers

Goals for further research are:

Study TiNiPd system by co-sputtering and employing the '50-50' composition rule.

Systematic exploration of palladium-containing film was inhibited during phase I by the lack of suitable targets. If an 8-inch Pd target is purchased and installed along with TiNi and Ti targets it will be possible to co-sputter TiNiPd film in the same manner as was successfully done with TiNiHf in Phase I.

Extend the usable temperature range of TiNiHf to 200°C for higher-temperature applications.

It is known that the transition temperature range of TiNiHf can be further increased by adding a larger fraction of Hf. Higher-temperature alloy that is ductile and machinable may be expected

to result if precisely the right composition is achieved, and this can be accomplished by methodically varying the composition and examining the thermo-mechanical properties of the resulting film.

Increase uniformity of film composition deposited on substrates to improve yield of product.

In a system with a platen that rotates under the sputtering source, geometrical effects result in thickness variation of film: a portion of the substrate that passes near the center of the target spends more time being exposed to the sputtering source and consequently has a higher effective sputtering rate. In addition to this effect, sputtering from an alloy target such as TiNi deposits material that has a radial variation of composition because of the differing sputtering rate of the atomic species. This effect is exacerbated in stationary DC magnetron sources because the material is removed largely from a narrow erosion ring.

These effects can be compensated by partially obscuring the targets with shields that shape the effective target area. This in turn reduces the effective sputtering rate, so higher power is required to achieve a specified deposition rate. If the sputtering rate is diminished, the time spent increases, and contamination from oxygen also increases.

Determine how best to measure composition of film.

The largest remaining problem is measurement of composition. It is desirable that the precise composition of 'good' material be determined so that larger volumes of material can be made by ingot casting and other processes and made into wires, plates, and tubes. It is necessary to measure the composition of targets and film samples to an accuracy of better than 1 percent, preferably to order of 0.1 %.

Several methods have been used for evaluation: SEM (WDS and EDS), Auger, and ICPMS. Microprobe analysis, which is a specialized form of scanning electron microscope, has been proposed but has not been used. Each of these methods has advantages and disadvantages. None has proven to reliably produce measurement of composition to the required accuracy, but it is the opinion of experts that microprobe, Auger, and ICPMS can achieve the required results, especially if measurement is made relative to a known standard of composition close to the sample under test.

Following is a summary of the knowledge gained regarding composition measurement from the Phase I study.

Scanning electron microscopy (SEM)

We have conferred with Bob Jones at Stanford University regarding the use of SEM for composition analysis.[4] The advice offered is that, provided a state-of-the-art WDS system is used a resolution of 2% may be achieved easily, and with care, 1%. Similarly, for EDS, 1% accuracy may be achieved with great care. See Appendix 1. Comparison measurements using a known standard or 'ranking' of adjacent samples can produce results accurate to a fraction of one percent.

In order to verify the precision of measurement with WDS, an analysis of two TiNi film samples was performed by Bob Jones at Stanford, and these confirm that it is indeed possible to measure to less than one percent absolute accuracy.

Two samples were examined. Both were from a wafer deposited from a TiNi target. One sample shows a halo, suggesting a high transition temperature. The other was from an area that was completely smooth. The take-off angle was 40 degrees relative to the beam; the beam energy was 15 kV.

From the smoother of the two samples, the average of 10 samples was 51.0 at% Ni and 49 at% Ti. The cloudy sample yielded an average of 48.4 at% Ni and 51.6 at% Ti. Although the second result is surprisingly high in Ti, these results are consistent with the observation of transition temperature correlated with a halo appearance. (It is also generally known that TiNi alloy that is slightly greater than 50 at% has a martensite structure at room temperature.) The tentative conclusion is that WDS is indeed capable of measuring absolute composition of TiNi film to less than one at%.

These results are consistent with the observation that the smoother sample has a low transition point due to excess Ni, and the 'cloudy' sample, being slightly rich in Ti, has a higher transition point.

A section of substrate across a wafer was analyzed by Ian Ward at CEA.[2] This specimen was from a wafer on which TiNiHf was deposited by co-sputtering. These results, presented in Table III above, are consistent with an absolute accuracy of about 1% for EDS spectroscopy with state-of-the-art equipment and technique.

Auger spectroscopy

A very limited study of samples using Auger spectroscopy were measured during Phase I by Walter Bockmann.[3] Two sets of measurements were made: one was on two samples of TiNi having differing compositions. The other was on a 5-sample group adjacent to the film measured by CEA. These results are still being interpreted and are therefore not presented in this document.

Inductively Coupled Plasma Mass Spectroscopy (ICPMS)

ICPMS is a costly procedure. The equipment is expensive, the sample preparation process is complex, and a high degree of skill is involved. We have enquired of several vendors. Only one was willing to undertake the measurements: South Dakota School of Mines & Technology (SDSMT). ICPMS is clearly capable of absolute measurements down to 0.1% based on results from Lawrence Livermore National Laboratory (LLNL) two years ago. During the Phase I performance period we were unable to get further measurements from LLNL because of heavy use by the National Ignition Facility program. [5]

A variety of samples of TiNi and TiNiHf were measured by Russ Lingenfelter at SDSMT using ICPMS. The results are included in Table V.

Table V

Comparison of Composition Measurements, Atomic %

Target identification		Intended Composition	ICPMS SDSMT	ICPMS LLNL	Chem. NASA	WDS Stanford
#1: Low-temp, TiNi (wt% Ni56, Ti44)	Ti	49.06	48.35			
	Ni	50.94	51.65			
#2: Hi-temp TiNi (wt% Ni55, Ti45)	Ti	50.07	52.39			
	Ni	49.93	47.61			
#3: TiNiHf (Popoff) (wt% Ti35, Ni55, Hf10)	Ti	42.4	29.48			
	Ni	54.3	36.181			
	Hf	3.25	6.819			
#4: TiNiHfCu (Danilov) (Wt% Ti33, Ni37, Hf25, Cu5)	Ti	44.8	40.978	39.496		
	Ni	40.97	45.068	45.811		
	Hf	9.11	9.641	9.884		
	Cu	5.12	4.313	4.809		
#5: TiNiPd (Armada) (wt% Ti37.23, Ni24.63, Pd38.14)	Ti	50	35.96		21.7	
	Ni	23	19.81		38	
	Pd	27	44.23		36.6	
	Other	0	0		3.7	
Selected film sample: Smooth, Low-Temp.	Ti					48.98
	Ni					51.02
Selected film sample: Textured, Hi-Temp.	Ti					51.61
	Ni					48.39

Conclusions

TiNiHf deposition from three targets (TiNi, Hf, Ni) was highly successful, meeting nearly all of the project objectives. TiNiHf samples having transition temperatures above 100°C and shape memory properties including ductility have been demonstrated. Valve actuator dies were fabricated by micromachining, and tested satisfactorily.

A novel three-target co-sputtering technique enabled us to produce film with less composition gradient than the previous experiments, but there still remains a significant gradient: In a worst case, Af temperatures varied across a wafer from 160°C down to lower than -50°C. This is attributed to variation in amount of material deposited on different parts of the wafer from purely geometric causes. It can be corrected by shielding the targets. Shields however reduce the

effective sputtering rate, so we need higher power sources. This is not within the scope of Phase I, but will be included in Phase II.

Stress-strain measurements reveal, on a limited sample, that the stress required for plastic deformation in the Martensite phase is higher for TiNiHf (300 MPa) than for binary TiNi (100 MPa). This may be due to precipitates formed during annealing, or these alloys may require higher temperatures for annealing than the binary material. Further study will be required.

A useful hypothesis that alloys of 50 at% Ni, 50 at%(Ti+Hf) should have good thermomechanical properties is supported by experimental results.[6] Experimentally all film with desirable thermomechanical properties contain about 50% Ti or Ti plus Hf and 50% Ni.

Deposition onto a heated substrate produced material that was crystalline but with poor mechanical properties. Columnar structure was observed in TiNi film deposited onto a hot (~500°C) substrate. Deposition at elevated temperature does not produce ductile material because of this columnar structure.

The characteristics of TiNiHfCu have not been studied extensively because no 8-inch targets made of alloys containing Cu were available. TiNiPd deposited had increased transition temperatures, but very limited ductility. TiNiPd experiments were not conclusive. No 8-inch targets containing Pd were available.

Measurement of composition was not accomplished to the accuracy required to verify correlation with thermomechanical behavior as determined by resistivity measurements. Satisfactory results (as precise as 0.1%) in measuring absolute atomic percent content have been achieved only with ICPMS. Measurement of composition of thin film material remains a problem. A means for measurement of absolute composition is essential if bulk materials are to be made. Meanwhile, for sputtered film, the correct composition can be achieved by co-sputtering from two or more targets.

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- [4] Bob Jones, Geballe Laboratory for Advanced Materials (LAM), Stanford University, Stanford CA 94305-4045. Tel. 650 725 1677 or 650 723 5374
- [5] Gary Johnson, Lawrence Livermore National Laboratory, tel. 925 423 0156. Private communication.
- [6] Anatoli Danilov, St. Petersburg, Russia, tel. 011 7 812 541 0698. Private communication, 1998.

Appendix A: Scanning Electron Microscope as a Tool for Composition Measurement

The scanning electron microscope is the most readily available of the systems used to measure composition of thin film samples. Can the SEM be used for analysis of ternary thin film alloy samples? The following is a brief review of some considerations in the application of SEM spectroscopy.

EDS measurement

The advantage of using energy dispersive spectrometry is that all components of a sample are measured simultaneously, so to first order effects such as voltage drift and physical shifting of the filament electron source affect all chemical species the same. Peak heights are measured, and the total counts within peaks are compared. Since the efficiency of x-ray generation differs for the species, the unknown sample should be compared with a sample of known composition for optimum resolution. EDS analysis is useful because trends can be seen by ranking of adjacent areas.

WDS measurement

In wave dispersive spectrometry, the peak to background ratio is high, of the order of several hundred, so background subtraction is generally unnecessary. But the stability of the system must be very high. Anything that varies with time (e.g. beam position, voltage, beam intensity, physical alignment of the beam/sample/analyzing crystal/detector) affects the reading. And only one chemical species can be measured at a time, so the physical and electrical conditions must be very nearly identical from minute to minute and hour to hour.

To achieve the finest resolution the following should be observed:

- Samples must always be well grounded.
- Samples surfaces must be smooth to micron finish.
- Stage must be straight, and take-off angle must be constant (usually 45 degrees for WDS)
- The same beam voltage should be used (20 kev recommended).
- To avoid dead time in the detector (2-3 microseconds), the counting rate should be kept below 10,000 counts/second, and long samples should be used, 20 seconds or 10,000 counts at least. (Standard deviation then is 100 counts)
- The beam spot size must be less than 1 micron. Interaction volume is about one micron cubed.
- Beam current at last aperture must be measured and used in computations or fed back to keep it constant.
- Filament changes shape with age, introducing steering errors: it is advisable to use as small a current as possible.
- Use feedback on filament current with a pair of crossed slits and a steering magnet.
- Keep machine running at all times, and keep temperature and other conditions constant.

- Do a calibration on every data sample. Use a Faraday cup that can be moved into beam and out again. Measure current before and after every sample.
- Implement a method of data collection so that records are kept automatically. This mean having a standard available at all times: on a shuttle that can be moved in and out of beam.
- Stabilize the power supplies. A suitable set of power supplies would cost \$50,000.

With these enhancements, a high-quality scanning electron microscope may achieve 1% absolute, less than 0.1 % on 'ranking' measurement.